



# Photochemical and enzymatic methanol synthesis from $\text{HCO}_3^-$ by dehydrogenases using water-soluble zinc porphyrin in aqueous media

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## ARTICLE INFO

### Article history:

Received 23 May 2008

Received in revised form 13 August 2008

Accepted 13 August 2008

Available online 22 August 2008

### Keywords:

$\text{CO}_2$  fixation

Methanol synthesis

Artificial photosynthesis

Biocatalysis

Photochemical reaction

## ABSTRACT

We studied the photochemical and enzymatic synthesis of methanol from  $\text{HCO}_3^-$  using formate dehydrogenase (FDH) isolated from *Candida boidinii*, aldehyde dehydrogenase (AldDH) and alcohol dehydrogenase (ADH) isolated from yeast, and the photoreduction of methyl viologen ( $\text{MV}^{2+}$ ) by the visible-light sensitization using zinc tetraphenylporphyrin tetrasulfonate (ZnTPPS) in the presence of triethanolamine (TEOA). When a sample solution containing ZnTPPS,  $\text{MV}^{2+}$ , FDH, AldDH, ADH, TEOA, and  $\text{NaHCO}_3$  in potassium phosphate buffer solution (pH 8) was irradiated, the amount of methanol produced increased with the irradiation time. After irradiation for 3 h,  $4.5 \mu\text{mol dm}^{-3}$  of methanol was produced from  $100 \mu\text{mol dm}^{-3}$   $\text{NaHCO}_3$ . The conversion ratio of  $\text{HCO}_3^-$  to methanol was approximately 4.5%. This result indicates that a system for the photochemical synthesis of methanol from  $\text{HCO}_3^-$  can be developed by using three dehydrogenases (FDH, AldDH, and ADH) and for the photoreduction of  $\text{MV}^{2+}$  through the photosensitization of ZnTPPS in aqueous media.

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## 1. Introduction

The fixation and utilization of  $\text{CO}_2$  are potential steps for realizing the catalytic reduction of  $\text{CO}_2$  [1–3]. Many researchers have attempted the electrocatalyzed reduction of  $\text{CO}_2$  using specific electrode materials [4]. Further, in studies on  $\text{CO}_2$  fixation, researchers have also investigated photocatalysis on titanium dioxide, silicon carbide, and strontium titanate surfaces [5,6]. However, these systems use ultraviolet irradiation and give very poor yields; hence, a highly efficient  $\text{CO}_2$  fixation system that uses visible-light is desired.

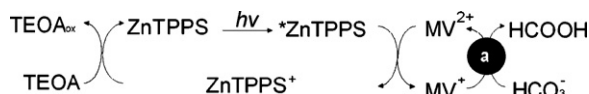
Visible-light-induced photoredox systems that consist of an electron donor, a photosensitizer, and an electron relay have been widely studied [7]. An effective photosensitizer is an essential component of such systems. Ruthenium(II) coordination compounds and porphyrins are widely used as effective photosensitizers in photoredox systems. Water-soluble zinc porphyrins such as zinc tetraphenylporphyrin tetrasulfonate (ZnTPPS) and zinc tetrakis (4-methylpyridyl) porphyrin (ZnTMPyP) exhibit strong absorption bands in the visible region (380–600 nm); hence, they are more widely used as photosensitizers than ruthenium(II) coordination compounds [8–11]. Further, biological and enzymatic  $\text{CO}_2$  fixation systems have also received considerable attention. For

example,  $\text{CO}_2$  can be reduced to formic acid by using formate dehydrogenase (FDH) and nicotinamide adenine dinucleotide dehydrogenase (NADH) [12]. Therefore, a homogeneous photochemical  $\text{CO}_2$  reduction system that combines the photoreduction of  $\text{NAD}^+$  through the photosensitization of water-soluble zinc porphyrin and ferredoxin- $\text{NADP}^+$  reductase (FDR) and the reduction of  $\text{CO}_2$  using FDH is established.

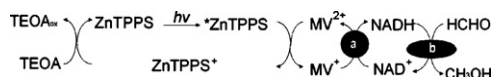
Some examples related to the photochemical  $\text{CO}_2$  reduction with enzymes have been reported. A  $\text{CO}_2$  fixation system based on malic acid synthesis from pyruvate and  $\text{HCO}_3^-$  with malic enzyme combined with the photoreduction of  $\text{NAD}^+$  by the photosensitization of chemically modified chlorophyll and FDR has also been reported [13]. The enzymatic synthesis of formic acid from  $\text{HCO}_3^-$  with FDH and the photoreduction of  $\text{MV}^{2+}$  using a system containing a ruthenium(II) coordination compound as a photosensitizer and mercaptoethanol as an electron donor has also been reported [14]. We have previously reported the visible-light-induced enzymatic synthesis of formic acid from  $\text{HCO}_3^-$  with FDH through the photosensitization of water-soluble zinc porphyrins, ZnTPPS or ZnTMPyP, in the presence of triethanolamine (TEOA) as an electron donor, as shown in Scheme 1 [15–17]. We have also reported a system for visible-light-induced methanol synthesis from formaldehyde using ADH isolated from *Saccharomyces cerevisiae* and  $\text{NAD}^+$  photoreduction through the visible-light photosensitization of ZnTPPS in the presence of TEOA, as shown in Scheme 2 [18,19]. In this system,  $0.38 \mu\text{mol dm}^{-3}$  of methanol is produced from  $16 \mu\text{mol dm}^{-3}$  of formaldehyde after irradiation

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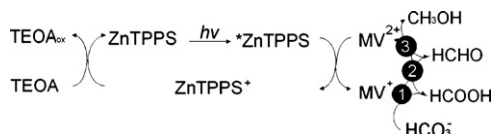
E-mail address: [amao@cc.oita-u.ac.jp](mailto:amao@cc.oita-u.ac.jp) (Y. Amao).



**Scheme 1.** Photochemical and enzymatic formic acid synthesis from  $\text{HCO}_3^-$  with FDH (a) and photoreduction of  $\text{MV}^{2+}$  with TEOA and ZnTPPS.



**Scheme 2.** Photochemical methanol synthesis from formaldehyde with alcohol dehydrogenase (ADH; b) via the photoreduction of  $\text{NAD}^+$  with diaphorase (a) using ZnTPPS photosensitization.



**Scheme 3.** Photochemical and enzymatic methanol synthesis from  $\text{HCO}_3^-$  with formate (1), aldehyde (2), and alcohol dehydrogenases (3) via the photoreduction of  $\text{MV}^{2+}$  using ZnTPPS photosensitization.

for 180 min. The conversion ratio of formaldehyde to methanol is approximately 2.3%. However, as shown in Scheme 2, the use of two electronic carrier molecules, methyl viologen and  $\text{NAD}^+$ , and the enzyme diaphorase complicates the reaction system. Since the NADH formed plays the same role as TEOA, the production efficiency of methanol will be lowered. Therefore, we propose the use of methyl viologen as the electron carrier and a dehydrogenase substrate. The photochemical synthesis of methanol from the  $\text{HCO}_3^-$  system, as shown in Scheme 3, is accomplished by adding aldehyde dehydrogenase (AldDH) and alcohol dehydrogenase (ADH) in the above-mentioned visible-light-induced formic acid synthesis system by the combination of Schemes 1 and 2. Although reactions shown in Schemes 1 and 2 that use each dehydrogenase, FDH and AldDH have been successfully carried out, the development of a methanol synthesis system using all the three dehydrogenases (FDH, ADH, AldDH), as shown in Scheme 3 is difficult, since it requires optimization of enzyme activity and stabilization of the intermediate, especially formaldehyde. Thus, considerable efforts have gone into the development of the methanol synthesis system shown in Scheme 3. Yoneyama and coworkers reported the electrocatalytic synthesis of methanol from a  $\text{CO}_2$ -saturated buffer solution using FDH and ADH [20]. We have previously reported in a communication letter, the development of photochemical and enzymatic methanol synthesis from  $\text{HCO}_3^-$  using FDH, AldDH, and ADH via the photoreduction of methyl viologen ( $\text{MV}^{2+}$ ) using ZnTPPS photosensitization [21]. However, the mechanism of this reaction has not yet been clarified.

In this paper, we describe a system for visible-light-induced methanol synthesis from  $\text{HCO}_3^-$  by using FDH, AldDH, and ADH, and  $\text{MV}^{2+}$  photoreduction through the visible-light photosensitization of ZnTPPS in the presence of TEOA as an electron donor in an aqueous medium.

## 2. Experimental

### 2.1. Materials

FDH from *Candida boidinii* and AldDH from yeast were obtained from Roche Co., Ltd. ADH from yeast was purchased from Oriental Yeast Co., Ltd. Tetraphenylporphyrin tetrasulfonate ( $\text{H}_2\text{TPPS}$ ) was purchased from Tokyo Chemical Industry Co., Ltd. Other chemicals were of analytical grade or of the highest grade available.

### 2.2. Synthesis of ZnTPPS

ZnTPPS was synthesized by refluxing  $\text{H}_2\text{TPPS}$  with approximately 10 times molar equivalent of zinc acetate in 100 ml methanol at 40 °C for 2 h. The insertion of the zinc ion into  $\text{H}_2\text{TPPS}$  was monitored by visible absorption spectroscopy. During the reaction, the intensity of the characteristic absorption band of ZnTPPS at 550 nm increased, while that of the absorption band due to  $\text{H}_2\text{TPPS}$  at 650 nm decreased gradually. After evaporation of the solvent, the product was dissolved in distilled water and used as such for the subsequent experiments. Although the excess zinc acetate was not removed from the ZnTPPS solution, it has been confirmed that zinc acetate has no influence on the subsequent photoreactions [22].

### 2.3. Enzyme activity

One unit of FDH activity was defined as the amount of enzyme required to convert 1.0  $\mu\text{mol}$  formic acid to  $\text{NaHCO}_3$  in 1 min in the presence of  $\text{NAD}^+$ . One unit of AldDH activity was defined as the amount of enzyme required to convert 1.0  $\mu\text{mol}$  formaldehyde to formic acid in 1 min in the presence of  $\text{NAD}^+$ . One unit of ADH activity was defined as the amount of enzyme required to convert 1.0  $\mu\text{mol}$  methanol to formaldehyde in 1 min in the presence of  $\text{NAD}^+$ .

### 2.4. Photoreduction of $\text{MV}^{2+}$

A solution containing ZnTPPS (0.1  $\mu\text{mol dm}^{-3}$ ),  $\text{MV}^{2+}$ , and TEOA (0.3  $\text{mol dm}^{-3}$ ) in 3.0 ml of 10  $\text{mmol dm}^{-3}$  potassium phosphate buffer (pH 8) was deaerated by six freeze–pump–thaw cycles. The sample solution was irradiated at 30 °C by a 200-W tungsten lamp (Philips) placed at a distance of 3.0 cm from the sample; this tungsten lamp was equipped with a Toshiba L-39 cut-off filter. The  $\text{MV}^+$  concentration was determined from the absorbance at 605 nm at a molar extinction coefficient of 13,000  $\text{mol}^{-1} \text{ dm}^3 \text{ cm}^{-1}$  [23].

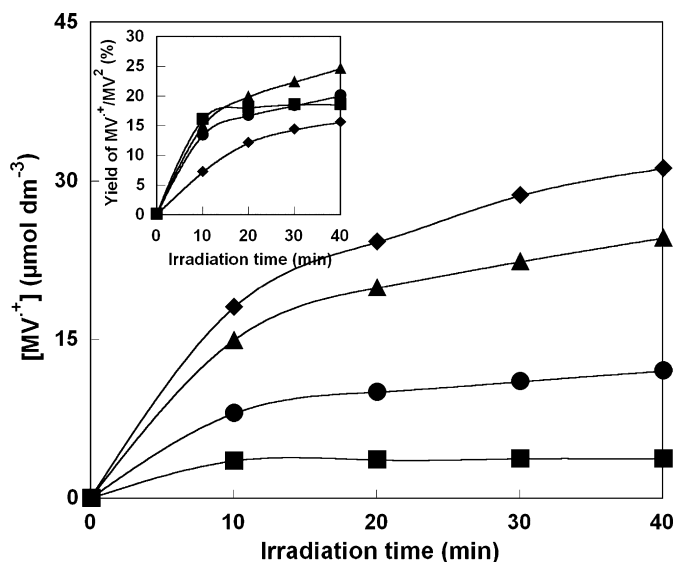
### 2.5. Enzymatic and photochemical methanol production

A sample solution containing ZnTPPS (0.1  $\mu\text{mol dm}^{-3}$ ),  $\text{MV}^{2+}$  (0.1  $\text{mmol dm}^{-3}$ ), TEOA (0.3  $\text{mol dm}^{-3}$ ), FDH, AldDH (12.5 units), and ADH (12.5 units) was deaerated by six freeze–pump–thaw cycles and then by flushing with argon gas for 5 min. The sample solution was irradiated after the addition of  $\text{NaHCO}_3$ . The amount of methanol produced was measured by gas chromatography (GC) using a 25% Sorbitol-Gasport B column (i.d.: 2 m  $\times$  3 mm; GL Sciences) attached to a Shimadzu GC-8A gas chromatograph (oven temperature: 100 °C; carrier gas:  $\text{N}_2$ ; flow rate: 21.8  $\text{ml min}^{-1}$ ). The by-products formed in the reaction were analyzed by high-pressure liquid chromatography (HPLC) with an electrical conductivity detector (Shimadzu CDD-10A<sub>VP</sub>) (column temperature: 40 °C; column: polystyrene sulfonate column, Shimadzu SCR-H; elutant: *p*-toluene sulfonic acid; flow rate: 0.8  $\text{ml min}^{-1}$ ).

## 3. Results and discussion

### 3.1. Photoreduction of $\text{MV}^{2+}$

The photoreduction of  $\text{MV}^{2+}$  is the most important step in photochemical synthesis of methanol from the  $\text{HCO}_3^-$  system. The reaction conditions required for obtaining the highest yield of the reduction product  $\text{MV}^+$  were investigated. The time dependence of the  $\text{MV}^+$  concentration in the system containing ZnTPPS,  $\text{MV}^{2+}$ , and TEOA for various  $\text{MV}^{2+}$  concentrations under visible-light irradiation

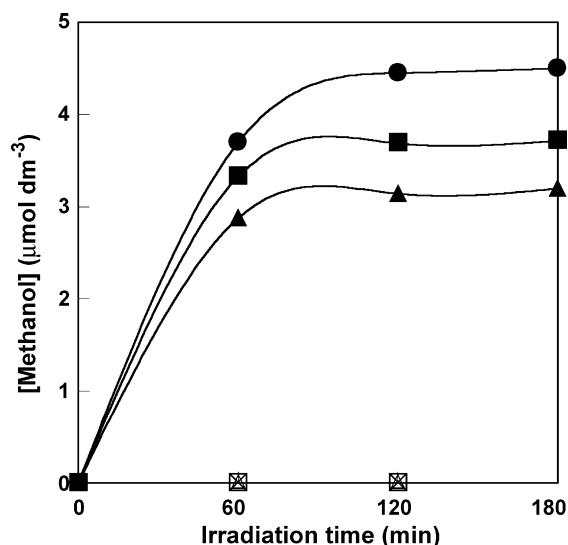


**Fig. 1.** Time dependence of  $MV^{2+}$  reduction under steady-state irradiation with visible-light by using a 200-W tungsten lamp placed at a distance of 3.0 cm from the sample solution. The solution contained TEOA ( $0.3 \text{ mol dm}^{-3}$ ), ZnTPPS ( $0.1 \text{ μmol dm}^{-3}$ ), and  $MV^{2+}$  in 3.0 ml of  $10 \text{ mmol dm}^{-3}$  potassium phosphate buffer (pH 7.0). Concentrations of  $MV^{2+}$ : squares,  $0.02 \text{ mmol dm}^{-3}$ ; circles,  $0.05 \text{ mmol dm}^{-3}$ ; triangles,  $0.1 \text{ mmol dm}^{-3}$ ; and diamonds,  $0.2 \text{ mmol dm}^{-3}$ . The inset indicates the time dependence of conversion yield of  $MV^{2+}$  to  $MV^+$ .

tion is shown in Fig. 1. The rate of  $MV^+$  formation increased with the concentration of  $MV^{2+}$ , as shown in Fig. 1. In contrast, the conversion yield of  $MV^{2+}$  to  $MV^+$  increased when the concentration of  $MV^{2+}$  reached  $0.1 \text{ mmol dm}^{-3}$  and then decreased, as shown in the inset of Fig. 1. FDH catalyzes both the reduction of  $HCO_3^-$  to formic acid and the oxidation of formic acid to  $HCO_3^-$ . The rate of reduction of  $HCO_3^-$  to formic acid is 20 times slower than that of oxidation of formic acid to  $HCO_3^-$  in this system. At high  $MV^{2+}$  concentrations,  $HCO_3^-$  was produced by the oxidation of formic acid with FDH. The conversion yield of  $MV^{2+}$  to  $MV^+$  is important for formic acid synthesis using the system shown in Scheme 1. Therefore, the optimum  $MV^{2+}$  concentration for methanol synthesis is  $0.1 \text{ mmol dm}^{-3}$ . After irradiation for 40 min,  $25 \text{ μmol dm}^{-3}$   $MV^+$  was produced. The reduction ratio of  $MV^{2+}$  to  $MV^+$  was approximately 25% after irradiation for 40 min.

### 3.2. Effect of FDH activity on methanol production

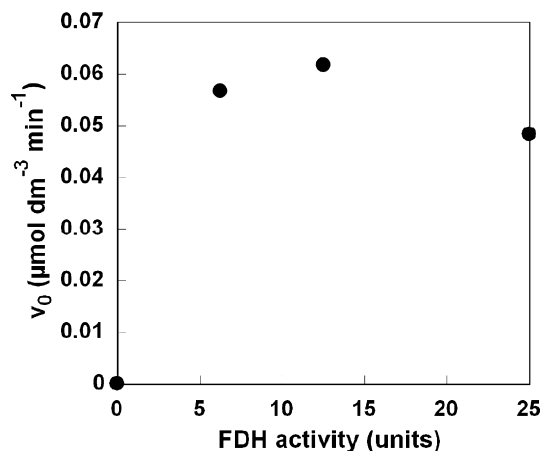
As the  $MV^{2+}$  photoreduction system was developed using the photosensitization of ZnTPPS, the photochemical methanol synthesis from  $HCO_3^-$  was attempted using FDH, AldDH, and ADH under the above-mentioned conditions. FDH catalyzes the reduction of  $HCO_3^-$  to formic acid as well as the oxidation of formic acid to  $HCO_3^-$ . As the rate of reduction of  $HCO_3^-$  to formic acid is 20 times slower than the rate of oxidation of formic acid to  $HCO_3^-$  in the system containing FDH, the synthesis of formic acid is an important step for methanol synthesis in this system. Initially, optimum FDH activity was determined under the following conditions: ZnTPPS ( $0.1 \text{ μmol dm}^{-3}$ ),  $MV^{2+}$  ( $0.1 \text{ mmol dm}^{-3}$ ), TEOA ( $0.3 \text{ mol dm}^{-3}$ ), FDH, AldDH (12.5 units), ADH (12.5 units), and  $NaHCO_3$  ( $0.1 \text{ mmol dm}^{-3}$ ) in potassium phosphate buffer solution (pH 8.0) irradiated at  $30^\circ\text{C}$  with a 200-W tungsten lamp. The FDH activity varied between 6.25 and 25 units. The rate of methanol formation when the sample solution was irradiated with a 200-W tungsten lamp for various durations is shown in Fig. 2. In all cases, the rate of methanol production increased with the irradiation time. Fig. 3 shows the relationship between the FDH



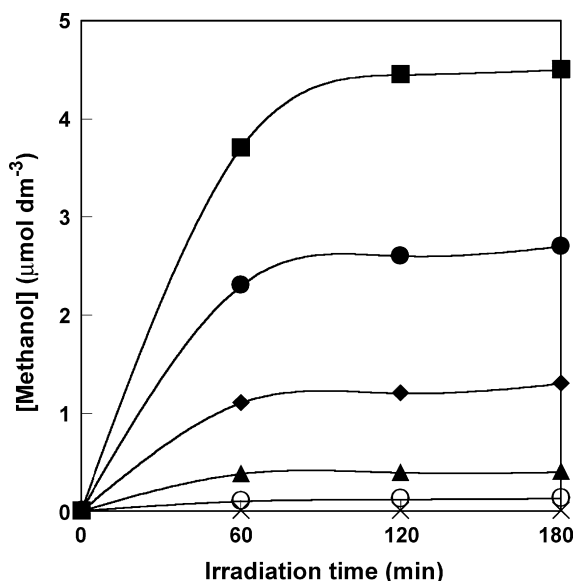
**Fig. 2.** Time dependence of methanol production with the system consisting of TEOA ( $0.3 \text{ mmol dm}^{-3}$ ), ZnTPPS ( $0.1 \text{ mmol dm}^{-3}$ ),  $MV^{2+}$  ( $0.1 \text{ mmol dm}^{-3}$ ),  $NaHCO_3$  ( $0.1 \text{ mmol dm}^{-3}$ ), FDH, AldDH (12.5 units), and ADH (12.5 units) in potassium phosphate buffer (pH 8.0) under steady-state irradiation at  $30^\circ\text{C}$ . FDH activity: closed squares, 6.25 units; closed circles, 12.5 units; and closed triangles, 25.0 units. X: no FDH, open triangles: no AldDH, open triangles: no ADH.

activity and the methanol production rate ( $v_0$ ). The  $v_0$  value was determined from the methanol concentration after irradiation for 60 min. The methanol concentration increased when the FDH activity was increased up to 12.5 units and then decreased. Therefore, the optimum activity of FDH for photochemical methanol synthesis is confirmed to be 12.5 units. At this FDH activity, the rate of methanol synthesis was  $0.061 \text{ μmol dm}^{-3} \text{ h}^{-1}$ . Thus, the methanol synthesis rate decreased when the FDH activity was more than 12.5 units owing to a decrease in the amount of formic acid. Thus, the methanol synthesis rate was found to increase with an increase in the FDH units owing to the increase in the production of formic acid.

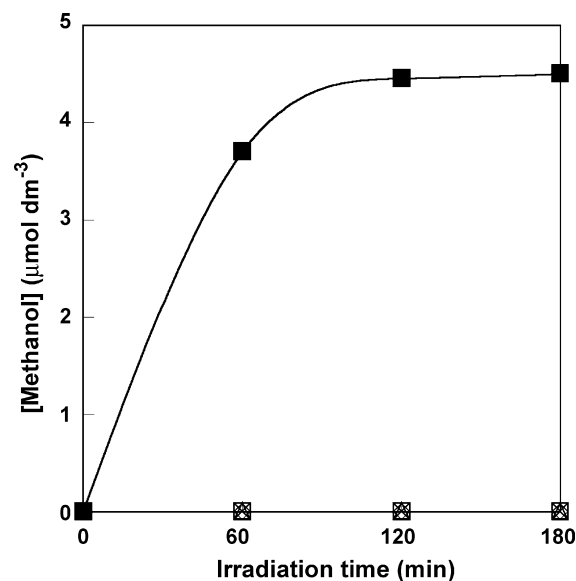
Next, we focused on the effect of three dehydrogenases (FDH, AldDH, and ADH) on the methanol synthesis. No methanol production was observed in the absence of FDH, AldDH, or ADH in above reaction system as shown in Fig. 2. Production of formic acid was observed with a system containing TEOA, ZnTPPS,  $MV^{2+}$ , FDH, and ADH (in the absence of AldDH). These results indicate that FDH, AldDH, and ADH, are necessary for methanol production and for catalyzing the reaction shown in Scheme 3.



**Fig. 3.** Relationship between FDH activity and  $v_0$ .



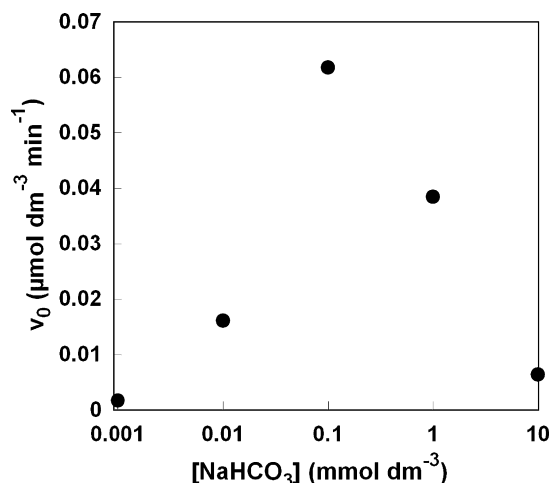
**Fig. 4.** Time dependence of methanol production with the system consisting of TEOA (0.3 mmol dm<sup>-3</sup>), ZnTPPS (0.1 μmol dm<sup>-3</sup>), MV<sup>2+</sup> (0.1 mmol dm<sup>-3</sup>), NaHCO<sub>3</sub>, FDH (12.5 units), AldDH (12.5 units), and ADH (12.5 units) in potassium phosphate buffer (pH 8.0) under steady-state irradiation at 30 °C. NaHCO<sub>3</sub> concentration: open circles, 0.001; diamonds, 0.01; squares, 0.1; circles, 1.0; and triangles, 10 mmol dm<sup>-3</sup>.



**Fig. 6.** Time dependence of methanol production with the system consisting of TEOA (0.3 mmol dm<sup>-3</sup>), ZnTPPS (0.1 μmol dm<sup>-3</sup>), MV<sup>2+</sup> (0.1 mmol dm<sup>-3</sup>), NaHCO<sub>3</sub> (0.1 mmol dm<sup>-3</sup>), FDH (12.5 units), AldDH (12.5 units), and ADH (12.5 units) in potassium phosphate buffer (pH 8.0) under steady-state irradiation at 30 °C (closed squares). Open squares: no irradiation, X: no FDH, open diamonds: no AldDH, and open triangles: no ADH.

### 3.3. Effect of NaHCO<sub>3</sub> concentration on methanol production

Next, let us focus on the effect of NaHCO<sub>3</sub> concentration on the methanol synthesis in a system containing ZnTPPS (0.1 μmol dm<sup>-3</sup>), MV<sup>2+</sup> (0.1 mmol dm<sup>-3</sup>), TEOA (0.3 mol dm<sup>-3</sup>), FDH (12.5 units), AldDH (12.5 units), ADH (12.5 units), and NaHCO<sub>3</sub> in potassium phosphate buffer (pH 8.0) solution irradiated at 30 °C by a 200-W tungsten lamp. The NaHCO<sub>3</sub> concentration was varied between 0.1 and 10 mmol dm<sup>-3</sup>. The rate of formation of methanol when the sample solution was irradiated for different irradiation times with a 200-W tungsten lamp is shown in Fig. 4. In all cases, the amount of methanol produced increased with the irradiation time. Fig. 5 shows the relationship between the NaHCO<sub>3</sub> concentration and  $v_0$ . The  $v_0$  value was determined from the methanol concentration after irradiation for 60 min. The methanol concentration increased when the NaHCO<sub>3</sub> concentration was increased up to 0.1 mmol dm<sup>-3</sup> and then decreased. Moreover, no methanol formation was observed in



**Fig. 5.** Relationship between NaHCO<sub>3</sub> concentration and  $v_0$ .

the absence of NaHCO<sub>3</sub>. Therefore, the optimum NaHCO<sub>3</sub> concentration was confirmed to be 0.1 mmol dm<sup>-3</sup> for the photochemical methanol synthesis. When the NaHCO<sub>3</sub> concentration was 0.1 mmol dm<sup>-3</sup>,  $v_0$  was 0.061 μmol dm<sup>-3</sup> h<sup>-1</sup>. Fig. 6 shows the rate of formation of methanol by using the system containing ZnTPPS (0.1 μmol dm<sup>-3</sup>), MV<sup>2+</sup> (0.1 mmol dm<sup>-3</sup>), TEOA (0.3 mol dm<sup>-3</sup>), FDH (12.5 units), AldDH (12.5 units), ADH (12.5 units), and NaHCO<sub>3</sub> (0.1 mmol dm<sup>-3</sup>) in potassium phosphate buffer solution (pH 8.0) irradiated at 30 °C a 200-W tungsten lamp. After irradiation for 3 h, the amount of methanol produced and the conversion yield of HCO<sub>3</sub><sup>-</sup> to methanol were estimated to be 4.5 μmol dm<sup>-3</sup> and 4.5%, respectively. In contrast, no methanol production was observed without irradiation (open squares shown in Fig. 6) and in the absence of HCO<sub>3</sub><sup>-</sup>. Thus, we confirmed that methanol is not produced from the oxidized TEOA, but from the reduction of HCO<sub>3</sub><sup>-</sup> by FDH, AldDH, or ADH (X, open diamonds, and triangles shown in Fig. 6). These results indicate that the photochemical synthesis of methanol from HCO<sub>3</sub><sup>-</sup> is possible by using FDH, AldDH, and ADH via the photoreduction of MV<sup>2+</sup> using ZnTPPS photosensitization.

The by-products formed in the reaction mixture were analyzed by GC and HPLC (with an electrical conductivity detector). Methanol and formaldehyde were detected by GC, while formic acid and ZnTPPS were detected by HPLC; no other by-product was detected. Moreover, the concentration of methanol produced was more than that of initial ZnTPPS concentration in all cases. For example, the amount of methanol production was estimated to be 0.0135 μmol after 180 min irradiation. It indicated that 0.0135 μmol of HCO<sub>3</sub><sup>-</sup>, that was 45 times the amount of ZnTPPS (0.3 nmol) in the sample solution, was reduced to methanol molecules. These results also suggest that the reaction shown in Scheme 3 proceeded catalytically. Although the reaction conditions shown in Scheme 3 were optimized, the methanol production was saturated with irradiation time. We previously reported the photochemical and enzymatic synthesis of formic acid from HCO<sub>3</sub><sup>-</sup> by using a system containing TEOA, water-soluble zinc porphyrin, MV<sup>2+</sup>, and FDH. In this system, formic acid production was also

saturated with the irradiation time [17]. Since FDH is light-sensitive, it may be deactivated after irradiation. To prevent the degradation of ZnTPPS and the dehydrogenases by near-UV light, wavelengths of less than 390 nm were blocked by using a Toshiba L-39 cut-off filter. When the FDH assay with the system containing  $\text{NAD}^+$ , FDH, and formic acid (see Section 2.2) was performed under irradiation, FDH was deactivated with an increase in the irradiation time. Thus, the methanol production was thought to be saturated due to the decrease in the formic acid supply caused by FDH deactivation.

#### 4. Conclusion

In conclusion, photochemical and enzymatic synthesis of methanol from  $\text{HCO}_3^-$  with three dehydrogenases (FDH, AldDH, and ADH) and  $\text{MV}^{2+}$  photoreduction by the visible-light photosensitization of ZnTPPS in the presence of TEOA were carried out. After irradiation for 3 h, the concentration of methanol produced from  $\text{HCO}_3^-$  and the conversion yield of  $\text{HCO}_3^-$  to methanol were estimated to be  $4.5 \mu\text{mol dm}^{-3}$  and 4.5%, respectively. This system could be further enhanced to convert  $\text{CO}_2$  into useful organic compound materials. Thus,  $\text{CO}_2$  has been effectively used to produce methanol through an environment-friendly process in aqueous media. The amount of methanol produced and turnover number of ZnTPPS and  $\text{MV}^{2+}$  are low. Further improvement in the amount of methanol produced and optimum conditions used in the reaction system, as shown in Scheme 3, are being studied in detail.

#### Acknowledgment

This work was partially supported by a special fund from The Japan Petroleum Institute.

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